California Environmental Protection Agency Department of Pesticide Regulation 1020 N Street, Room 161 Sacramento, CA 95814

# STUDY 166: PROTOCOL FOR MONITORING ACUTE AND CHRONIC TOXICITY IN THE SACRAMENTO RIVER WATERSHED: WINTER 1997-98 November 20,1997

#### I. INTRODUCTION

The Department of Pesticide Regulation (DPR) has a responsibility to ensure that pesticides are distributed and used in a safe manner. California law requires DPR to consider and encourage the use of pest control products and procedures that reduce the risk to human and environmental health. The Department has developed a Pest Management Strategy to increase the adoption of reduced-risk pest management practices. The reduced-risk management practices involve economically viable techniques that either currently exist or can be developed through research and education that will lower the health and environmental risks of controlling pests. DPR is charged with evaluating the effectiveness of it's efforts to facilitate the adoption of these practices. One measure of success of this strategy would be decreasing incidences of pesticide toxicity in the rivers and waterways of California.

The Sacramento River is the largest river in California both in flow and in drainage area (Figure 1). From Mount Shasta in the north to the Sacramento-San Joaquin Delta in the south the river flows for 327 miles and drains approximately 27,000 square miles including agricultural, urban and undeveloped land (Domalgalski and Brown, 1994). The Sacramento River provides 35% of the State's water supply, both drinking and agricultural, and is also an important resource for recreation and wildlife (Reynolds, et al., 1993). The primary source of water entering the system is surface runoff from the Sierra Nevada Mountains to the east and the Cascade Range to the north (CSLC, 1993). Runoff from rain events occurring in the Sacramento Valley provides significant short term increases in river flow. Seasonal rains occur from October to March with little significant rain from June to September. River flow during the summer is composed of dam releases of snow melt water for agricultural, recreational and wildlife purposes.

In the Sacramento Valley, the organophosphorus insecticides diazinon and methidathion are the primary dormant season insecticides used on stone fruit and nut

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crops (DPR 1993; DPR 1994; DPR 1995). The dormant season spray application period coincides with the bulk of the seasonal rainfall, providing the potential for these pesticides to wash off target areas and migrate with surface runoff to the Sacramento River. Pesticide use reports (DPR 1993-1995) indicate that the majority of dormant spray insecticides are applied along the Feather River north of the Bear River and along the Sacramento River in northern Butte and Glenn Counties and southern Tehama County. The primary dormant spray OP insecticides, diazinon and methidathion, are applied in nearly identical areas (Figures 2 and 3) and these areas remain fairly stable from year to year. Runoff from orchard areas west of the Sacramento River chiefly flows into the Colusa Basin Drain which enters the Sacramento River at Knights Landing (Figure 4). Runoff from dormant spray areas east of the Sacramento River principally flows into Butte Creek, which has been engineered to drain into the Sutter Bypass via the Butte Slough. Runoff from the west side of the Feather River also drains into the Sutter Bypass. During periods of normal flow, the Sutter Bypass enters the Sacramento River via the Sacramento Slough at Karnak. During periods of high flow, the Sutter Bypass channel fills completely with runoff from this area plus water diverted from the Sacramento River. This flow merges with the Feather River eight miles prior to entering the Sacramento River, forming a two mile wide channel which inundates the Sacramento Slough. During floods, a large portion of the flows for the Sacramento River and the Sutter Bypass/Feather River will be diverted into the Yolo Bypass. Runoff from areas east of the Feather River drains into the Feather River above Nicolaus.

A one year DPR study and a three year U.S. Geological Survey (USGS) study of the Sacramento River have shown that most diazinon and methidathion detections were observed during the dormant spray season (MacCoy et. al. 1995; Nordmark, 1995). No other organophosphate (OP) or carbamate (CB) insecticides were detected. Atrazine and simazine have also been detected during winter monitoring by the USGS. These detections occur almost exclusively in conjunction with rain events indicating that rain runnoff is the primary source of pesticides entering the rivers. Toxicity has been found at Gilsizer Slough, which drains some of the area west of the Feather River and flows into the Sutter Bypass. *Ceriodaphnia dubia* mortality was 100% in five of the seven consecutive weekly samples. This toxicity appeared related to levels of pesticides detected in four of the samples with an inderminate cause of toxicity in the fifth sample (Foe and Sheipline, 1993).

During the winter of 1996-97, DPR conducted toxicity monitoring at sites along the Sacramento River and Sutter Bypass (Nordmark, 1997). Extensive flooding occurred in January which greatly affected river discharges and modified the

sampling schedule. No chronic toxicity or reproductive impairment was found at the Sacramento River at Bryte site and no acute toxicity was found at the Sutter Bypass site. A single diazinon pulse lasting up to eight days was detected in the Sacramento River in late-January and diazinon was also detected in the Sutter Bypass at this time. Methidathion was detected in a single sample from the Sacramento River and from the Sutter Bypass. These detections appeared rain event related. Diazinon was detected in a second pulse lasting up to two weeks in late-February in the Sutter Bypass, but did not appear to be related to any storm event.

In this study we will continue to look at acute toxicity to C. *dubia* in a small watershed where the discharging waters do not contain major inputs from municipal or industrial sources. We will also investigate the potential for chronic toxicity in a section of the Sacramento River downstream of major dormant spray insecticide inputs in the watershed. Selected herbicides will also be monitored as recommended in the memo: (Goh 1997) "Category and recommendation of currently registered pesticides for surface water monitoring duringFY97-98." Long term monitoring of acute and chronic toxicity will help scientists at DPR evaluate the effectiveness of programs designed to decrease the runoff of dormant spray insecticides and selected herbicides.

# II. OBJECTIVES

The objective of this study is to monitor the occurrence of acute and chronic toxicity in the Sacramento River watershed during the dormant spray season. Additionally, levels of specific organophosphate and carbamate insecticides and selected herbicides which have a potential to enter the Sacramento River with surface runoff will also be monitored. A companion study will be established to monitor pesticide levels and toxicity in the San Joaquin River.

#### III. PERSONNEL

This project will be conducted by the Environmental Hazards Assessment Program (EHAP) under the general direction of Don Weaver, Ph.D., Senior Environmental Research Scientist (Supervisor). Key personnel are listed below:

Project Leader: Craig Nordmark Field Coordinator: DeeAn Jones Senior Scientist: John Troianno, Ph.D.

Study Design/Data Analysis: Terre11 Barry, Ph.D.

Contractor (Toxicity Tests): Charlie Huang, Ph.D., California Dept. of Fish and Game

Chemist: Jean Hsu, Hsiao Feng, California Dept. of Food and Agriculture

Questions concerning this project should be directed to Pat Dunn at: (916) 324-4100 Fax: (916) 324-4088

# IV. STUDY PLAN

Sampling for acute toxicity will be conducted from a bridge across the east channel of the Sutter Bypass at the Karnak pumping station, as this site receives water that is predominantly agricultural (Figure 4). In the event of flooding at Karnak, the backup acute sampling site will be from the levee at Kirkville Road. Sampling for chronic toxicity will be conducted on the Sacramento River from the Alamar Marina dock as this site receives discharge from all the major agricultural tributaries (Figure 4) but is above the discharge of the largely non-agricultural American River and the urban runoff of the City of Sacramento. Discharge records are available for both the Karnak and Alamar sites from nearby gauging stations. This information will be used to correlate any changes in chemical concentrations to fluctuations in flow and may be useful for modeling efforts should they be undertaken.

Monitoring will commence prior to the onset of the dormant spray season (early December 1997) and continue through the second week of March 1998. Background samples will be collected for one week, beginning prior to dormant spray applications, then monitoring will resume once applications have begun and continue until no later than March 20, 1998. Additional data collection will include *in-situ* measurements of water pH and temperature, dissolved oxygen, and specific conductance.

# V. SAMPLING METHODS

Acute toxicity sampling will be conducted twice per week at Karnak. Sampling for chronic toxicity will be conducted weekly on the Sacramento River at Alamar. One chronic sample constitutes the collection of samples on days zero, two and four of each week (e.g. Monday, Wednesday and Friday). Water collected on those days will be delivered the following day to the laboratory for testing and sample renewal. Chemical analysis will be performed on each sample collected for both acute and chronic tests. Selected OP and CB pesticides will be analyzed in three analyses. Selected herbicides will also be analyzed in a fourth analysis (Table 1). The herbicides are not expected to reach levels where they would contribute to C. *dubia* 

toxicity, but will be monitored to look for possible effects on other aquatic life (Table 2).

At each sampling site, water will be collected from as close to center channel as possible using a depth-integrated sampler (D-77) with a 3-liter Teflon@ bottle and nozzle. Sampling at the Karnak site may be done from the stream bank with a grab pole when bridge access is deemed unsafe. The grab pole will consist of a new glass bottle at the end of a three meter pole. When the Karnak site is flooded water from the Sacramento and Feather Rivers backs up to the site. In that case, samples will be drawn from the levee at Kirkville Road, approximately 10 miles upstream. Surface water subsamples will be composited temporarily in a stainless steel container until the appropriate volume of water has been collected. The composited sample will be stored on wet ice until delivered to the processing facility at West Sacramento. Immediately upon arrival at the processing facility, the composite sample will be split into 1 -liter amber glass bottles, using a Geotech@ 1 O-port splitter, then sealed with Teflon@ lined caps. The organophosphate and carbamate chemical analysis samples will be preserved by acidification with 3N hydrochloric acid to a pH between 3.0 to 3.5. At this pH, most OP and CB pesticides are sufficiently preserved with the exception of diazinon. Therefore, diazinon and the herbicides will be analyzed from separate, unacidified, split samples. Samples submitted for toxicity tests will not be acidified. Sufficient water will be collected at each sampling event to provide approximately four liters for chemical analysis, two liters for toxicity testing, and any additional water required for quality control (QC) and backup samples.

Split samples for chemical analysis will be transported on wet ice to the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry within three days of collection. Split samples for toxicity testing will be delivered on wet ice to the California Department of Fish and Game (CDFG) Aquatic Toxicity Laboratory within 24 hours of collection. CDFG will measure and record other parameters of the split samples including totals of ammonia, alkalinity, hardness, and specific conductivity as part of their toxicity testing.

# VI. TOXICITY TESTING AND CHEMICAL ANALYSIS

Toxicity testing conducted by CDFG Aquatic Toxicity Laboratory (ATL) will follow current USEPA procedures using the cladoceran *Ceriodaphnia dubia* (U.S. EPA, 1993). The CDFG-ATL has been accredited by the California Department of Health Services' Laboratory Accreditation Program. Acute toxicity will be determined

using a 96-hour, static renewal bioassay in undiluted sample water. Chronic toxicity will be determined using a 7-day bioassay of undiluted sample water with C. *dubia* and will follow current USEPA guidelines (U.S. EPA, 1994). For example, test organisms used in chronic testing will be subjected to sample water from day zero on the following day (day 1). Sample water collected on days two and four will then replace test water on days three and five, respectively, All bioassays must commence within 36 hours of sample collection. Data will be reported to the project leader as percent survival on each day for the duration of the tests.

Chemical analysis will be performed by CDFA Center for Analytical Chemistry. The reporting limit will be the lowest concentrations of analyte that the method can detect reliably in a matrix blank. The reporting limits for this study are listed in Table 1. Chemical analytical methods will be provided in the final report. The total number of samples is presented below.

# **Number of Toxicity Tests** 2 acute tests/week x 11 weeks of study 22 11 1 chronic test per week x 11 weeks of study Total number of toxicity tests <u>33</u> **Number of Chemical Analyses** 4 (OP, CB, diazinon and herbicides) per acute toxicity sample: 4 analyses x 2 acute toxicity sampling events/week x 11 weeks 88 4 (OP, CB, diazinon and herbicides) per chronic toxicity sampling event: 4 analyses x 3 chronic sampling events (=1 chronic sample)/week x 11 weeks 132 Subtotal <u>220</u> **Quality Control** Continuing QC (approx. 10% of total chemical analyses) 22 Total number of chemical analysis samples 242

# VII. QUALITY ASSURANCE/QUALITY CONTROL

#### Chemical Analysis

Quality control will be conducted in accordance with Standard Operating Procedure QAQC001 .OO. Ten percent of the total number of primary analyses will be submitted with field samples as rinse blanks, matrix blanks, and blind matrix spikes.

# VII. DATA ANALYSIS

Toxicity data will be used to establish baseline information on the occurrence of acute or chronic events at these sites. A correlation matrix will be established to identify potential relationships between measured environmental parameters, discharge, toxic events, and chemical concentrations. Further analysis may include multivariate analysis, depending on preliminary analysis results.

# IX. TIMETABLE

Site Survey and Selection September 1997

Field Sampling December 2-6, 1997 and January 5 through March 13, 1997

Preliminary Report Aug. 1998

## X. REFERENCES

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- U.S. Environmental Protection Agency. Draft. Pesticide Ecological Effects Database. For information contact: Brian Montague, Ecological Effects Branch, Environmental Fate and Effects Division (H7507C), U. S. Environmental Protection Agency, 401 M St. S.W., Washington, D.C.,20460.